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Comparison for the compositions of fast and slow pyrolysis oils by NMR characterization

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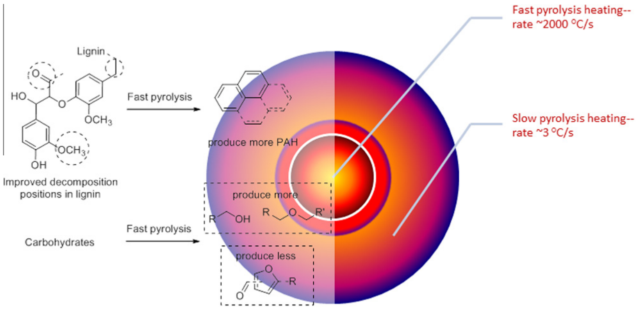
HIGHLIGHTS

- Pyrolysis of SW kraft lignin and pine wood were examined.
- Various NMR and GPC were used to characterize various pyrolysis oils.
- Fast pyrolysis improved cleavage of methoxyl, aliphatic C—C and carbonyl bonds.
- Fast pyrolysis produced more PAH from lignin.
- Molecular weight of fast pyrolysis oils increased by ~100%.

GRAPHICAL ABSTRACT


Lignin
HO
O
O
OCH3
OCH3
OH
Improved decomposition positions in lignin
Fast pyrolysis
produce more PAH
Carbohydrates
Fast pyrolysis
produce more
R
OH
R
O
R'
produce less
O
O
-R
Fast pyrolysis heating--rate ~2000 °C/s
Slow pyrolysis heating--rate ~3 °C/s

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ABSTRACT

The pyrolysis of softwood (SW) kraft lignin and pine wood in different pyrolysis systems were examined at 400, 500 and 600 °C. NMR including quantitative ^{13}C and Heteronuclear Single-Quantum Correlation (HSQC)–NMR, and Gel Permeation Chromatography (GPC) were used to characterize various pyrolysis oils. The content of methoxyl groups decreased by 76% for pine wood and 70% for lignin when using fast pyrolysis system. The carbonyl groups also decreased by 76% and nearly completely eliminated in 600 °C pine wood fast pyrolysis oil. Compared to the slow pyrolysis process, fast pyrolysis process was found to improve the cleavage of methoxyl groups, aliphatic C—C bonds and carbonyl groups and produce more polyaromatic hydrocarbons (PAH) from lignin and aliphatic C—O bonds from carbohydrates. Another remarkable difference between fast and slow pyrolysis oils was the molecular weight of fast pyrolysis oils increased by 85–112% for pine wood and 104–112% for lignin.

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1. Introduction

The use of biomass for renewable energy production is of growing importance in satisfying environmental and societal concerns over fossil fuel usage today and in the future (Ragauskas et al., 2006). Biomass and biomass components can be used in a variety of ways to provide energy, including direct combustion, gasification and pyrolysis which can directly produce a liquid fuel precursor (Bridgwater et al., 1999). Some research works have studied the influences of the flow rate of carrier gas, sample particle size, heating rate and temperature on the pyrolysis process (Aho et al., 2013; Butterman and Castaldi, 2010; Debdoubi et al., 2006; Demiral et al., 2012; Demiral and Şensöz, 2006; Ferdous et al., 2002, 2001; Linder et al., 1983; Maiti et al., 2007; Pütün et al., 2007; Şensöz and Can, 2002; Su et al., 2012; Thangalazhy-Gopakumar et al., 2011; Tsai et al., 2006; Wang et al., 2008; Yoder et al., 2011). Among various parameters, heating rate has been reported as the primary one and investigated by many researchers (Bridgwater, 1999; Bridgwater et al., 1999; Mohan et al., 2006). Most recently, Bridgwater (2012) provided a review of fast pyrolysis of biomass. Typical weight yields for liquid, solid and gas products obtained by different thermal conversion process such as fast, intermediate, carbonization, gasification, torrefaction have been summarized. In addition, various fast pyrolysis reactors have been compared. The cause and effects of some challenging properties for the

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pyrolysis oils have also been investigated. It is well known that the higher heating rate of pyrolysis of biomass will provide higher liquid yield and it is beneficial for the thermal treatment of various biomasses including esparto (Debdoubi et al., 2006), pine wood (Şensöz and Can, 2002), pistachio shell (Pütün et al., 2007), and corncob (Demiral et al., 2012). However, some researchers (Pütün et al., 2007; Tsai et al., 2006) reported that there is no linear relationship between the heating rate and the yield of liquid products, and a very high heating rate may also decrease the yield of pyrolysis oil. Compare to the influence of heating rate on the yields of pyrolysis products, only a few researchers have investigated the effects of heating rate on chemical components of pyrolysis oils. On the basis of GC–MS analysis, Thangalazhy-Gopakumar et al. (2011) indicated that the contents of ketones, furans, toluene and phenols in pine wood and switchgrass pyrolysis oils increase when the heating rate elevated from 50–2000 °C/s. Debdoubi et al. (2006) examined the influence of heating rate on the components of pyrolysis oil produced from esparto. They indicated that the H/C ratio increased and O/C decreased in a higher heating rate produced pyrolysis oil. The authors also characterized the pyrolysis oils by ^{1}H NMR and the results showed that there was less aliphatic–aliphatic type of hydrogen when the heating rate increased. In contrast, the contents of aliphatic–oxygen and aliphatic–aromatic type hydrogen in the pyrolysis oil increased when employed higher heating rate. Tsai et al. (2006) pyrolyzed rice straw, sugarcane bagasse and coconut shell with different heating rates and found that the pH values of pyrolysis oil relatively increased with increasing heating rate. It has also been reported (Meng et al., 2012; Westerhof et al., 2012) that a pre-thermal treatment before fast pyrolysis process of biomass could improve the properties of pyrolysis oil.

The previous work in Ragauskas' group (Ben and Ragauskas, 2011b) characterized chemical components in the pyrolysis oils produced from slow pyrolysis (heating rate is ~2.7 °C/s) of softwood (SW) kraft lignin and found that the aliphatic OH, carboxyl, methoxyl group and ether bond in the lignin are the primary target functional groups to decompose during the pyrolysis. The general goal of this work was to examine the effects of different pyrolysis processes on the composition of pyrolysis products. It has been reported (Mohan et al., 2006) that there are only about 40% of pyrolysis oil could be analyzed by GC–MS. To fully analyze the whole portion of pyrolysis oils, this study used NMR and GPC to analyze pyrolysis liquid products produced from softwood kraft lignin and pine wood with different pyrolysis systems.

2. Materials and methods

All reagents used in this study were purchased from VWR International or Sigma–Aldrich (St. Louis, MO) and used as received. Lignin was isolated from a commercial USA softwood kraft pulping liquor. Wood chips used in this study were acquired from a 15-year old Loblolly pine tree from the southeastern US. Detailed information about this material has been reported by Huang et al. (2011). The wood chips were refined with a Wiley mill through a 0.13 cm screen and the resulting fine powder was stored at 0 °C.

2.1. Lignin separation and purification

Lignin was isolated from a commercial softwood kraft pulping liquor following published methods (Ben and Ragauskas, 2011b). In brief, the cooking liquor was filtered through filter paper and the filtrate was treated with EDTA-2Na$^+$ (0.50 g/100.0 mL liquor) and stirred for 1 h. The liquor was adjusted to a pH value of 6.0 with 2.00 M H_2SO_4 and stirred vigorously for 1 h. The liquors were then further acidified to a pH of 3.0 and frozen at −20 °C. After thawing, the precipitates were collected on a medium sintered glass funnel and washed three times with cold water by suspending the precipitates in the water and stirring vigorously at 0 °C for 1 h. The precipitates were collected, air dried, and soxhlet extracted with pentane for 24 h. The solid product was air dried and further dried under high vacuum at 45 °C for 48 h. The resulting purified kraft lignin sample was stored at −5 °C.

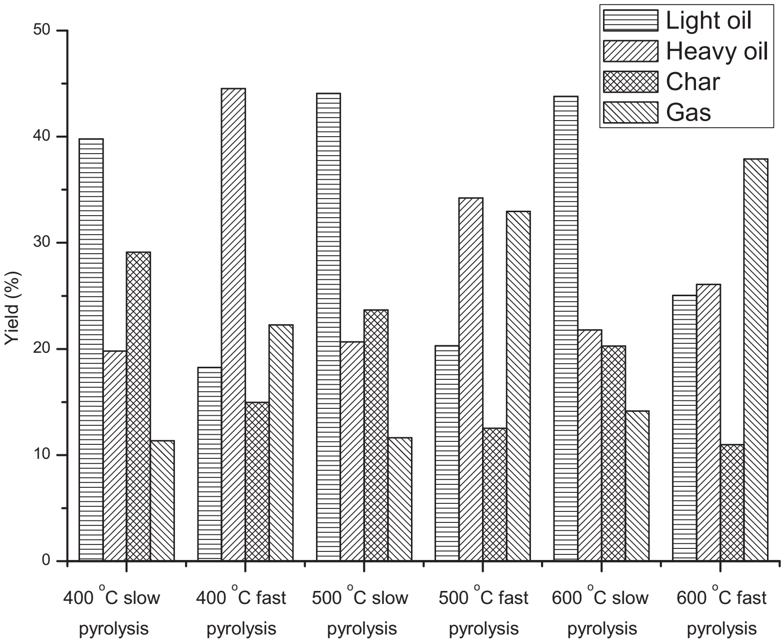

Fig. 1a. Yields of light oil, heavy oil, char and gas for the fast and slow pyrolysis of pine wood at different temperatures. The slow pyrolysis data were reported in previous work (Ben and Ragauskas, 2011b).

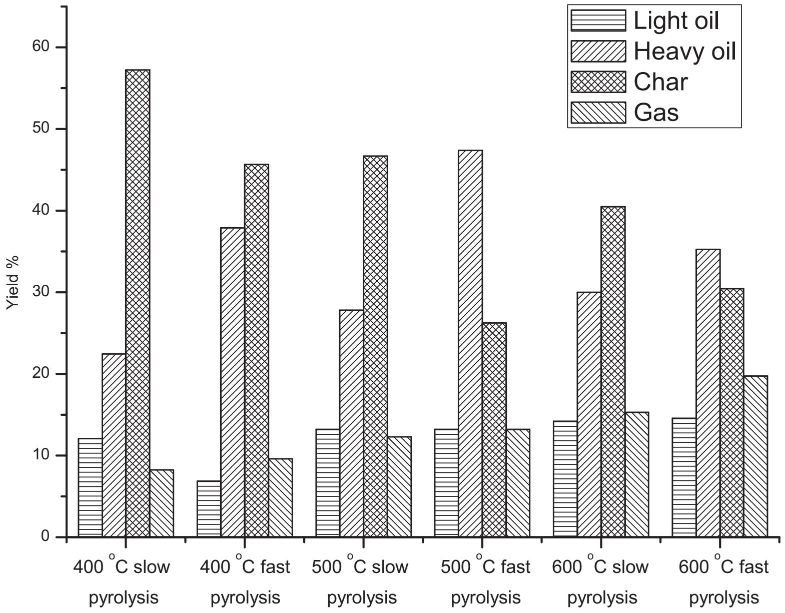

Fig. 1b. Yields of light oil, heavy oil, char and gas for the fast and slow pyrolysis of softwood kraft lignin at different temperatures. The slow pyrolysis data were reported in previous work (Ben and Ragauskas, 2011a).

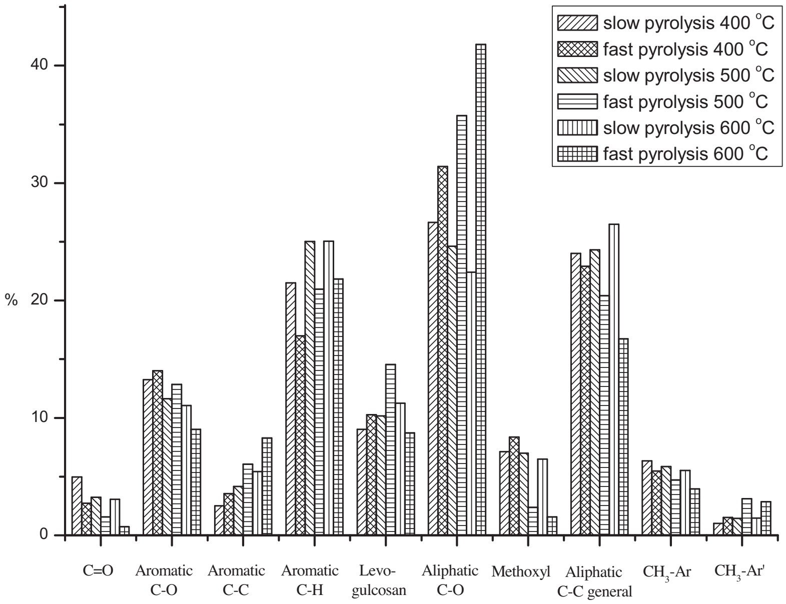

Fig. 2a. Integration results for the heavy oils produced by fast and slow pyrolysis of pine wood at different temperatures, detected by quantitative ^{13}C NMR. The results were shown as the percentage of carbon.

2.2. Equipment and process of pyrolysis

2.2.1. Slow pyrolysis system

The slow pyrolysis system used in this work is shown in Fig. S1 (see Fig. S1 in the supporting material). Pyrolysis experiments were conducted in a quartz pyrolysis tube heated with a split-tube furnace. Typically, the pyrolysis sample (4.00 g) was placed in a quartz sample boat that was then positioned in the center of a pyrolysis tube. A K-type thermal couple was immersed in the sample powder during the pyrolysis to measure the heating rate by a Parr@ temperature controller (model 4842). The pyrolysis tube was flushed with nitrogen gas and the flow rate was adjusted to a value of 500 mL/min and then inserted in the pre-heated furnace (ATS applied test systems, INC, series 3210). The outflow from pyrolysis was passed through two condensers, which were immersed in liquid N_2. Upon completion of pyrolysis, the reaction tube was removed from the furnace and allowed to cool to room temperature under constant N_2 flow. The condensers were then removed from liquid nitrogen. The pyrolysis char and oil were collected for subsequent chemical analysis. In general, the liquid products contained two immiscible phases referred to as heavy and light oil. The light oil was acquired by decantation and the heavy oil was recovered by washing the reactor with acetone followed by evaporation under reduced pressure. Char yields were determined gravimetrically and gas formation was calculated by mass difference.

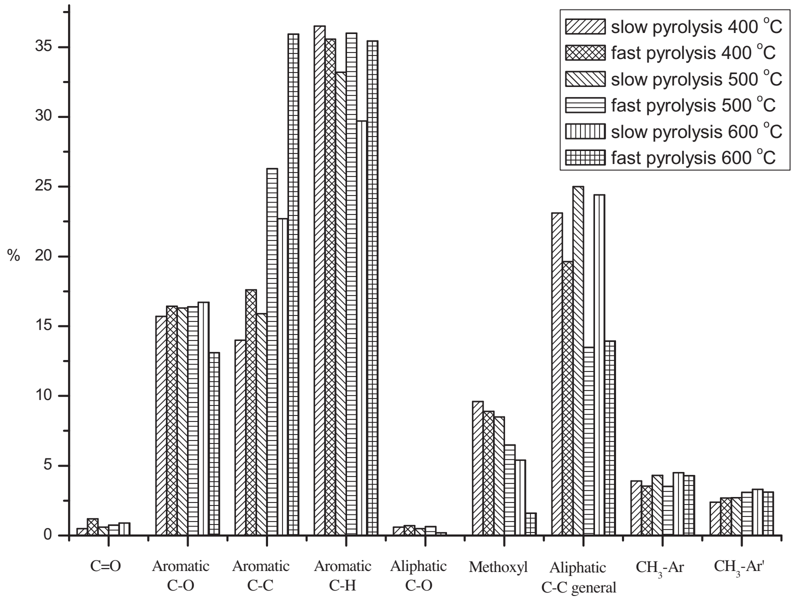

Fig. 2b. Integration results for the heavy oils produced by fast and slow pyrolysis of softwood kraft lignin at different temperatures, detected by quantitative ^{13}C NMR. The results were shown as the percentage of carbon. The slow pyrolysis data were reported in previous work (Ben and Ragauskas, 2011b).

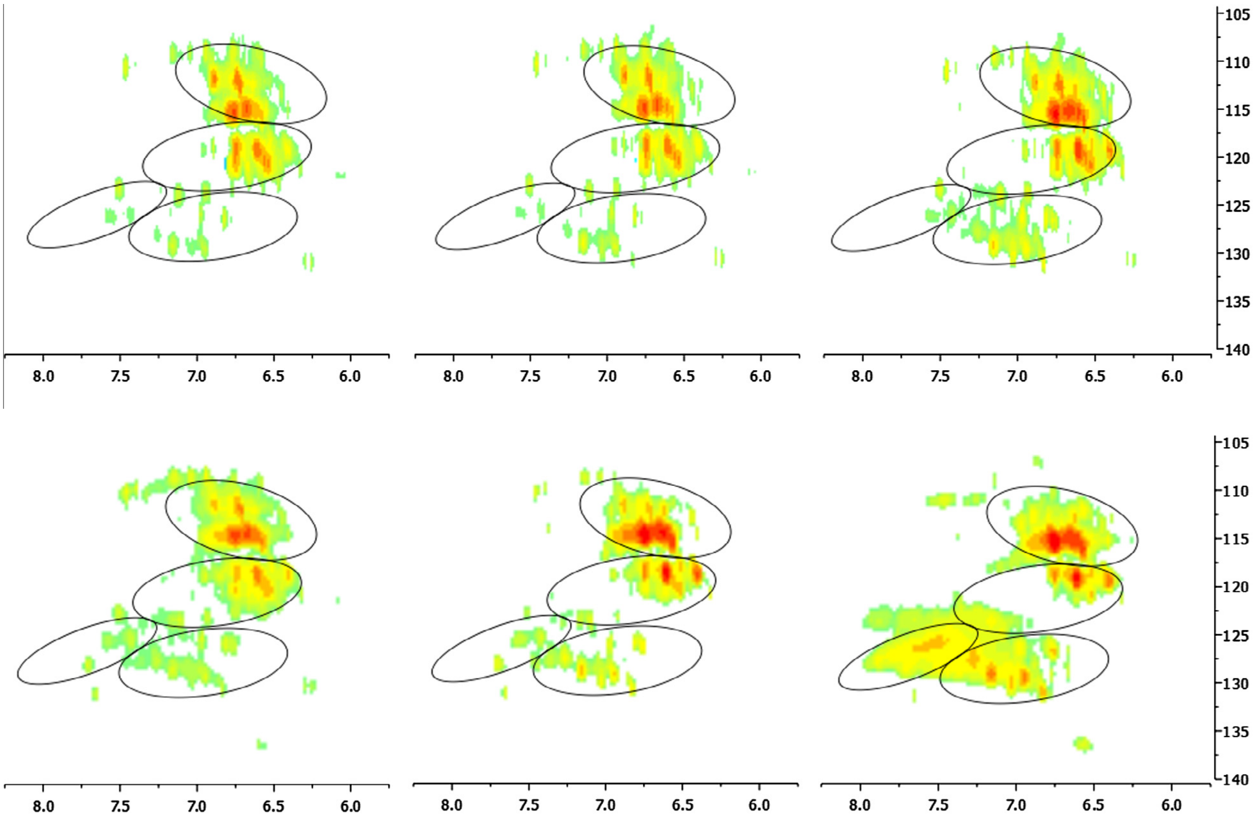

Fig. 3a. Aromatic C—H bonds in the HSQC–NMR spectra for the pyrolysis oils produced by pyrolysis of SW kraft lignin in different pyrolysis systems, from left top to right bottom is slow pyrolysis at 400, 500 and 600 °C, and fast pyrolysis at 400, 500 and 600 °C. The slow pyrolysis data were redrawn from previous work (Ben and Ragauskas, 2011a). The assignments (see supporting information for detail) represent C—H bonds at ortho or para position of a phenol; in a PAH or at meta position of a phenol (from top to bottom).

2.2.2. Fast pyrolysis system

The fast pyrolysis system used in this work is shown in Fig. S2. Typically, the pyrolysis sample (~100 mg/feed $*$ 30 feeds; manually controlled feeding, one feed/min) was fed into a small (r = 1.5 cm, h = 15 cm) fast stirred (200 rpm) pyrolysis reactor, which was immersed in the pre-heated sand bath, heated by a Corning® hot plate (model: PC-620D). The temperature was controlled by a K-type thermal couple, which was inserted into the reactor and connected to a Parr® temperature controller (model 4842). The pyrolysis reactor was flushed with pre-heated nitrogen

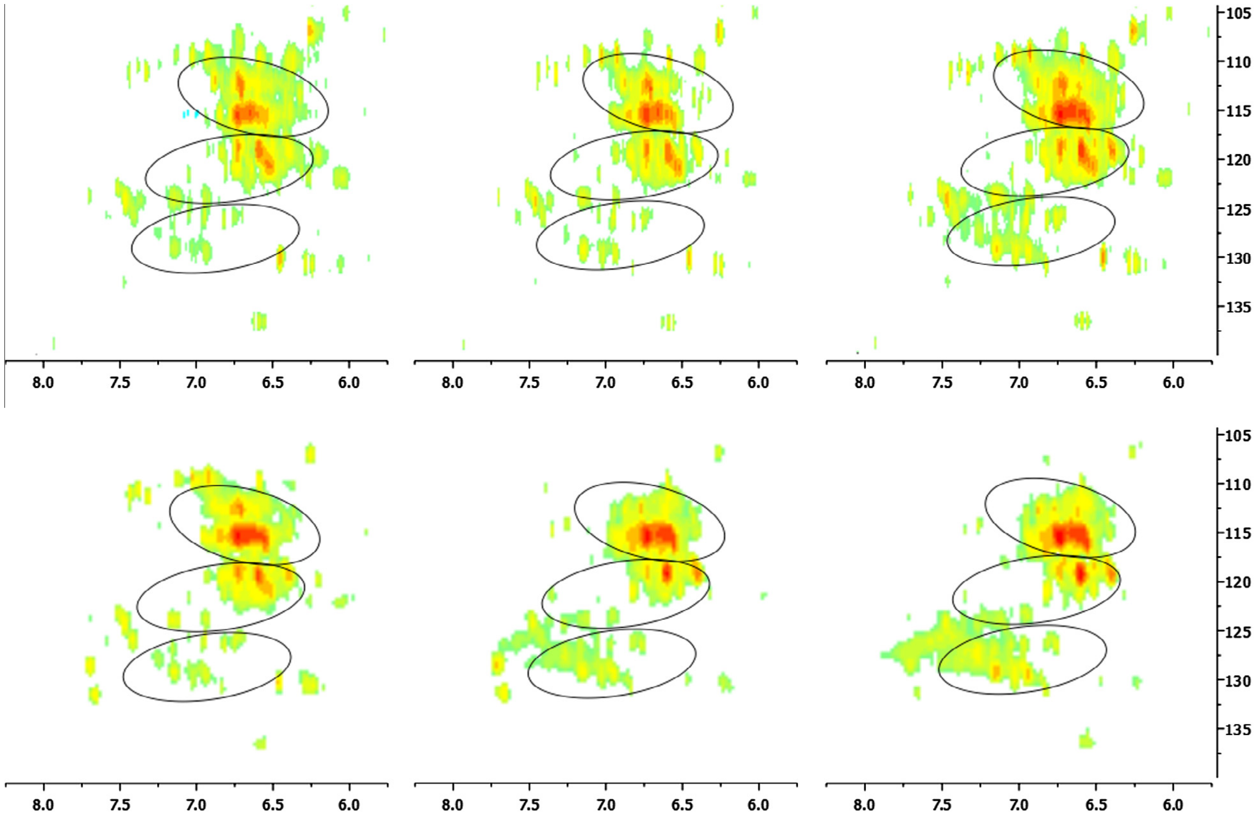

Fig. 3b. Aromatic C—H bonds in the HSQC–NMR spectra for the pyrolysis oils produced by pyrolysis of pine wood in different pyrolysis systems, from left top to right bottom is slow pyrolysis at 400, 500 and 600 °C, and fast pyrolysis at 400, 500 and 600 °C. The slow pyrolysis data were redrawn from previous work (Ben and Ragauskas, 2011a). The assignments (see supporting information for detail) represent C—H bonds at ortho or para position of a phenol; and at meta position of a phenol (from top to bottom).

gas and the flow rate was adjusted to a value of 500 mL/min. The biomass sample was heated up to the target temperature when it lands at the bottom of the reactor, the heating rate is ~2000 °C/s. The outflow from pyrolysis was passed through two condensers, which were immersed in liquid N_2. Upon completion of pyrolysis, the reactor was removed from the sand bath and allowed to cool to room temperature under constant N_2 flow. The condensers were then removed from liquid nitrogen. The pyrolysis char and oil were collected for subsequent chemical analysis. In general, the liquid products contained two immiscible phases referred to as heavy and light oil. The light oil was acquired by decantation and the heavy oil was recovered by washing the reactor with acetone followed by evaporation under reduced pressure. Char yields were determined gravimetrically and gas formation was calculated by mass difference.

2.3. Characterization of pyrolysis oils by GPC

The weight average molecular weight (M_w), number average molecular weight (M_n) and molecular weight polydispersity of the heavy oils were determined by GPC analysis following literature methods (Ben and Ragauskas, 2011b). Prior to GPC analysis, the heavy oil samples were dissolved in THF (1 mg/mL) and filtered through a 0.45 μm syringe filter. The samples were injected into a Polymer Standards Service (PSS) Security 1200 system featuring Agilent HPLC vacuum degasser, isocratic pump, refractive index (RI) detector and UV detector (270 nm). Separation was achieved with four Waters Styragel columns (HR0.5, HR2, HR4, HR6) using THF as the mobile phase (1.0 mL/min) with injection volumes of 30 μL. Data collection and processing were performed using PSS WinGPC Unity software. Molecular weights (M_n and M_w) were calibrated against a polystyrene calibration curve. The calibration curve was created by fitting a third order polynomial equation to the retention volumes obtained from a series of narrow molecular weight distribution polystyrene standards (i.e., 7.21×10^3, 4.43×10^3, 1.39×10^3, 5.80×10^2 Da), dioctyl phthalate (M_w = 390 g/mol), 2,2′-dihydroxy-4,4′-dimethoxyl-benzophenone (M_w = 274 g/mol), 2-phenylhydroquinone (M_w = 186 g/mol), phenol (M_w = 94 g/mol) and acetone (M_w = 58 g/mol). The curve fit had an R^2 value of 0.998.

2.4. Characterization of pyrolysis oil by NMR

2.4.1. Quantitative ^{13}C NMR

All NMR spectral data reported in this study were recorded with a Bruker Avance/DMX 400 MHz NMR spectrometer. Quantitative ^{13}C NMR were acquired using 100.0 mg heavy oil dissolved in 450 μL DMSO-d_6 employing an inverse gated decoupling pulse sequence, 90° pulse angle, a pulse delay of 5 s for heavy oils and 6000 scans at room temperature with a line-broadening (LB) of 5.0 Hz (Ben and Ragauskas, 2011b).

2.4.2. Characterization of pyrolysis oil by HSQC–NMR

HSQC–NMR were acquired using 100.0 mg pyrolysis oil dissolved in 450 μL DMSO-d_6 employing a standard Bruker pulse sequence "hsqcetgpsi.2" with a 90° pulse, 0.11 s acquisition time, a 1.5 s pulse delay, a $^1J_{C–H}$ of 145 Hz, 48 scans and acquisition of 1024 data points (for ^1H) and 256 increments (for ^{13}C). The ^1H and ^{13}C pulse widths are $p1$ = 11.30 μs and $p3$ = 10.00 μs, respectively. The ^1H and ^{13}C spectral widths are 13.02 ppm and 220.00 ppm, respectively. The central solvent peak was used for chemical shift calibration. HSQC data processing and plots were

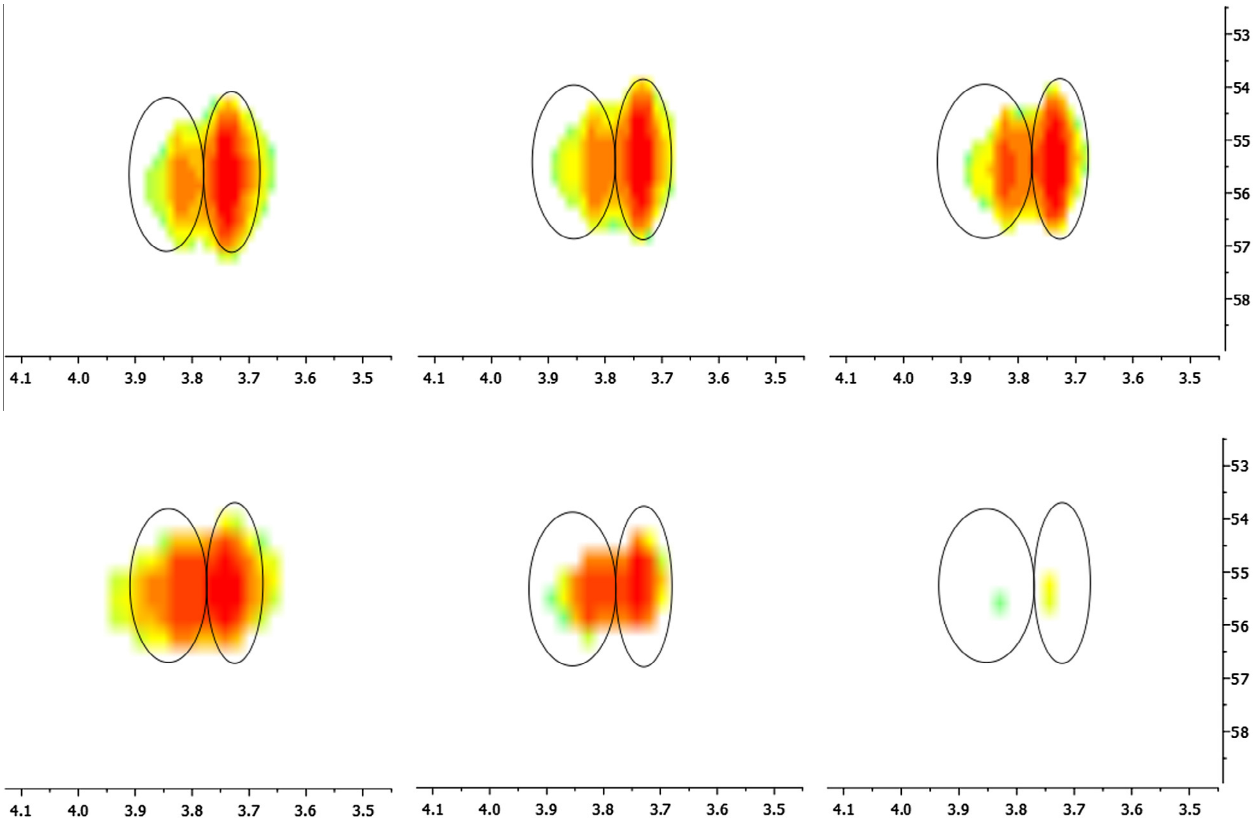

Fig. 3c. Methoxyl groups in the HSQC–NMR spectra for the pyrolysis oils produced by pyrolysis of SW kraft lignin in different pyrolysis systems, from left top to right bottom is slow pyrolysis at 400, 500 and 600 °C, and fast pyrolysis at 400, 500 and 600 °C. The slow pyrolysis data were redrawn from previous work (Ben and Ragauskas, 2011a). The assignments (see supporting information for detail) represent a methoxyl group with or without a hydroxyl group or ether bond in the ortho position (from left to right).

carried out using MestReNova v7.1.0 software's default processing template and automatic phase and baseline correction.

3. Results and discussion

3.1. Yields of pyrolysis products

The yields from pyrolyzing a softwood kraft lignin and pine wood with different pyrolysis systems at 400, 500 and 600 °C are summarized in Figs. 1a and 1b. The results indicate for both lignin and pine wood, fast pyrolysis process produced less char but more gas than the slow pyrolysis. The higher gas yield for the fast pyrolysis process indicates that higher heating rate could improve the decomposition of small pyrolysis oil components to gas products. The yields for liquid, solid and gas products shown in Figs. 1a and 1b are comparable with literature reports (Beis et al., 2010; Nowakowski et al., 2010). In addition, under the same thermal treatment temperature, fast pyrolysis could provide more heavy oil but relatively less light oil. It has been reported that the major component in the light oil is water (Ben and Ragauskas, 2011b). Therefore, for the usage as a biofuel and/or a bio-chemical precursor, heavy oil performs more better. Compared to slow pyrolysis, fast pyrolysis system could provide 125% more heavy oil from pine wood and 70% more heavy oil from lignin. Furthermore, different pyrolysis processes not only affect the yield of heavy oil but also influence the optimal temperature to produce maximum yield of heavy oil. Compared to the slow pyrolysis process, the temperature of highest yield of pine wood heavy oil shifted from 500 to 400 °C for fast pyrolysis process. Correspondingly, this temperature shift from 600 to 500 °C for pyrolysis of lignin. To explain the significant difference of the yields between fast and slow pyrolysis process, the pyrolytic behaviors of biomass major components between fast and slow pyrolysis process will be further discussed after characterization of pyrolysis oils.

3.2. Quantitative ^{13}C NMR analysis of pyrolysis oils

To characterize all the functional groups for the heavy oils, a detailed analysis was accomplished using ^{13}C NMR. The ^{13}C NMR chemical shift assignment ranges are based on previous work (Ben and Ragauskas, 2011b). The integration results for the heavy oils are summarized in Figs. 2a and 2b. The significant difference between fast and slow pyrolysis oil is the content of methoxyl groups. This content decreased by 76% for pine wood and 70% for lignin when using fast pyrolysis system at 600 °C, which indicates that fast pyrolysis process will improve the cleavage of methoxyl groups. The carbonyl groups also decreased by 76% and was nearly completely eliminated in the 600 °C pine wood fast pyrolysis oil, which indicates that the pine wood fast pyrolysis oil has lower acidity. Similarly, Tsai et al. (2006) pyrolyzed rice straw, sugarcane bagasse and coconut shell at different heating rate and found that the pH values relatively increased with increasing heating rate. There are more aliphatic C—O bonds in the pine wood fast pyrolysis oil than the slow pyrolysis oil. At 600 °C this type of bond increased by 86% when employed the fast pyrolysis system. Similarly, Debdoubi et al. (2006) examined the influence of heating rate on the components of pyrolysis oil produced from esparto. The authors characterized the pyrolysis oils by ^{1}H NMR and the results showed that there was less aliphatic–aliphatic but more aliphatic–oxygen and aliphatic–aromatic type of hydrogen when the heating rate increased. In contrast with pine wood pyrolysis oils, the

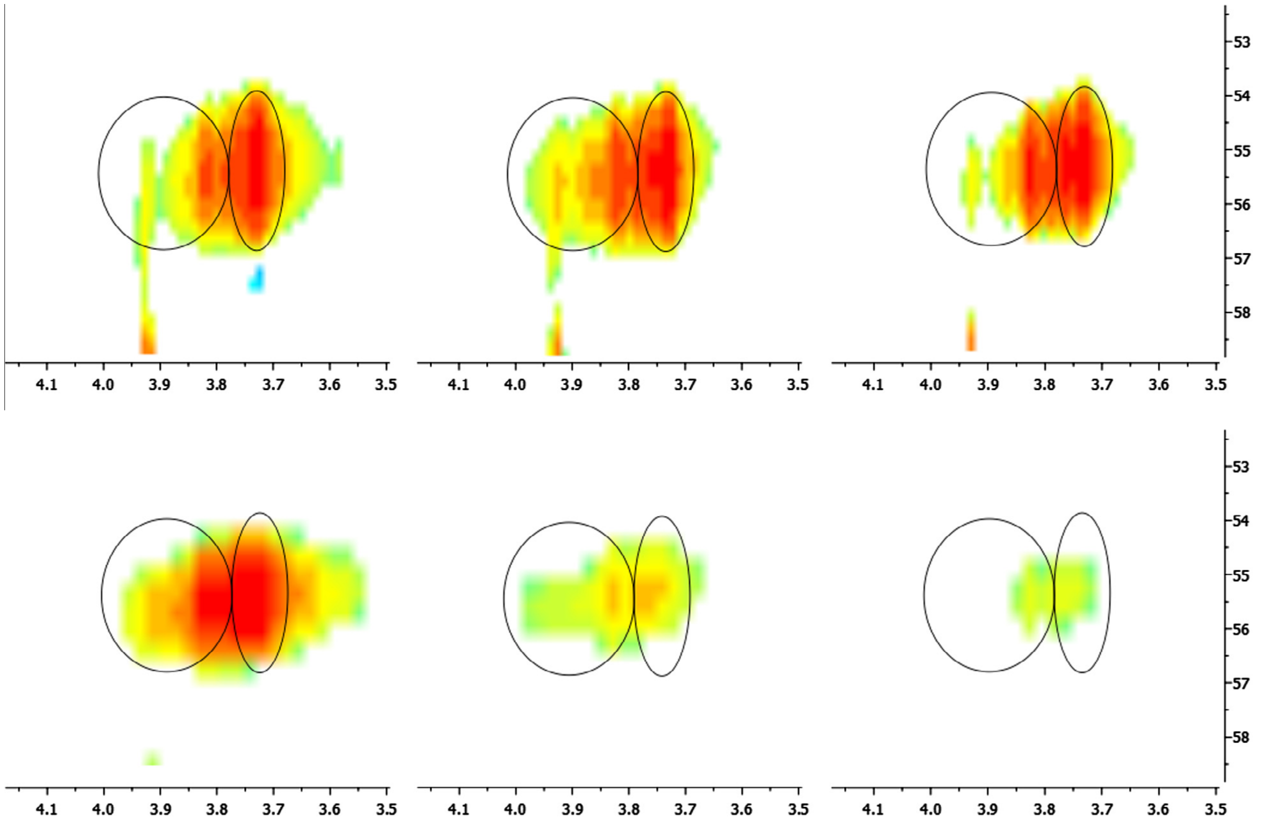

Fig. 3d. Methoxyl groups in the HSQC–NMR spectra for the pyrolysis oils produced by pyrolysis of pine wood in different pyrolysis systems, from left top to right bottom is slow pyrolysis at 400, 500 and 600 °C, and fast pyrolysis at 400, 500 and 600 °C. The slow pyrolysis data were redrawn from previous work (Ben and Ragauskas, 2011a). The assignments (see supporting information for detail) represent a methoxyl group with or without a hydroxyl group or ether bond in the ortho position (from left to right).

contents of aliphatic C—O bonds in both fast and slow lignin pyrolysis oils are very limited which indicates that different heating rate has relatively less effects on cleavage of aliphatic C—O bonds in the lignin structure. Therefore, the remarkable higher percentages of aliphatic C—O bonds in pine wood fast pyrolysis oil should be related with the carbohydrates portion in the biomass. The DEPT-135 analysis (Fig. S3 in the supporting material) shows that most of aliphatic C—O bonds (chemical shift from ~60–100 ppm) have a secondary carbon which indicate that most of these aliphatic C—O bonds in pine wood fast pyrolysis oil belong to the primary alcohol or ether bond and produced from carbohydrates components. In addition, compared to the lignin slow pyrolysis oils, there are much more aromatic carbons in the fast pyrolysis oils, especially at higher pyrolysis temperature. However, the content of aromatic carbons in the pine wood fast pyrolysis oil is lower than the slow pyrolysis oil. Considering the significantly increased amount of primary alcohols and ether bonds in the pine wood fast pyrolysis oil, the higher heating rate may prefer to convert carbohydrates to the aliphatic C—O bonds rather than aromatic rings. Another trend that could be observed from ^{13}C NMR data is that for both pine wood and lignin, compared to the slow pyrolysis oils, fast pyrolysis oils have remarkably more aromatic C—C bonds. Nevertheless, for both lignin and pine wood, the content of aliphatic C—C bonds decreased when employed fast pyrolysis process, which indicates that higher heating rate could improve the cleavage of aliphatic C—C bonds. Interestingly, for high temperature lignin fast pyrolysis oil, the percentages of aromatic C—C bonds are almost three times higher than the aliphatic C—C bonds, which indicate that most of these increased aromatic C—C bonds should belong to the polyaromatic hydrocarbons or biphenyl structures. In summary, the fast pyrolysis process could improve the cleavage of methoxyl groups, aliphatic C—C bonds and carbonyl groups and produce more polyaromatic hydrocarbons (PAH) from lignin and aliphatic C—O bonds from carbohydrates. The major influences of fast pyrolysis process on the pyrolysis products are summarized in Fig. S4.

3.3. HSQC–NMR analysis of pyrolysis oils

The HSQC–NMR spectrum for the pyrolysis oils produced from fast and slow pyrolysis of SW kraft lignin and pine wood are shown in Figs. 3a–3d. Compared to the slow lignin pyrolysis oil, there are more aromatic C—H bonds in the fast pyrolysis oil. Furthermore, the content of PAH also increased in the fast pyrolysis oils, especially in the high temperature oil, which is consistent with ^{13}C NMR results. In contrast, the fast pine wood pyrolysis oils contain relatively less aromatic C—H bonds than the slow pyrolysis oil. For both lignin and pine wood pyrolysis oils, there are much less methoxyl groups in the fast pyrolysis oils than the slow pyrolysis oils, which is also supported by ^{13}C NMR. By employing high temperature fast pyrolysis process, the methoxyl groups in both lignin and pine wood pyrolysis oils were nearly complete eliminated. Interestingly, there are relatively more rearranged methoxyl groups in the pyrolysis oils, which indicate the rearranged methoxyl groups (no hydroxyl group or ether bond in the ortho position) show some resistances for the decomposition compared to the native methoxyl groups (with a hydroxyl group or ether bond in the ortho position).

3.4. GPC analysis of pyrolysis oils

The number average and weight average molecular weights (M_n and M_w) for the pyrolysis oils produced from SW kraft lignin and pine wood by different pyrolysis treatments are summarized in

Fig. S5a and Fig. S5b. Compared to slow pyrolysis oils, GPC analysis indicates that the molecular weights of fast pyrolysis oils increase by 85–112% for pine wood and 104–112% for lignin. Therefore, fast pyrolysis process produced more liquid products; however, there was a significant increase in the molecular weight of the fast pyrolysis oils, which will bring more challenges for subsequent upgrading processes. For both fast and slow pyrolysis oils produced from pine wood, the molecular weights increased with increasing pyrolysis temperature. Slow pyrolysis of lignin also exhibited this trend; however, for the fast lignin pyrolysis oils, the molecular weight for the pyrolysis oil produced at 600 °C is lower than 500 °C. The HSQC and ^{13}C NMR also indicated that there are much more condensed aromatic C—C bonds which belong to the PAH in the high temperature lignin fast pyrolysis oil.

4. Conclusion

In summary, compare to the slow pyrolysis treatment, the fast pyrolysis process could provide higher yield of organic liquid products, which could be used as precursor of biofuel and bio-based chemical. Furthermore, fast pyrolysis process also improves the cleavage of several functional groups in the pyrolysis oil. However, the higher content of PAH and molecular weight for the fast pyrolysis oil will bring barriers for the following upgrading process.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2013.07.151.

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